

LOW-TEMPERATURE NO_x REMOVAL FOR FLUE GAS CLEANUP

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INTRODUCTION

A wide range of NO_x control processes for electric utilities are under investigation to compete with the current processes such as selective catalytic reduction (SCR). Although SCR using NH₃ is effective for NO reduction, the process suffers from many disadvantages [1]. In addition, current SCR processes must be located at places within the flue gas treatment process where temperatures are near 400 °C. Retrofitting SCR into these locations in the plant is costly because space and access in many power plants are extremely limited [2]. Therefore, there is a need to develop NO_x control technologies that can be located downstream of the particulate control device, near the stack, where temperatures are around 150 °C.

This study investigates the low-temperature selective reduction of NO with hydrocarbons under simulated flue gas conditions over carbon and carbon-supported catalysts. NO oxidation to NO₂ was also investigated as a way of making NO more reactive with hydrocarbons or easier to be removed by absorption at these temperatures.

EXPERIMENTAL

Four active carbon samples including type GI of Barnebey & Sulcliffe Corp. (GI), GmbH from Carbo-Tech (GmbH), PCB from Calgon (PCB), and Rheinbraun AG (AG) and one active carbon fiber (Osaka) provided by Professor Machida (Kyushu U.) were used in this experiment. All the granules were broken into 16/30 mesh particles followed by drying at 120 °C overnight. The carbon-supported catalysts were prepared by pore volume impregnation. The impregnated catalysts were first dried under vacuum at room temperature for 2 h, then at 60 °C for 2 h and 80 °C overnight. All catalysts were treated with 150 cm³/min of helium at 400 °C for 1 h before reaction. The schematic of the experimental system used in this study is the same as shown in the authors' previous report [3]. NO reduction was tested with 400 cm³/min of 0.1% NO, 4% O₂, 8% H₂O, and hydrocarbons in He over 7 g of catalysts. NO oxidation was carried out with 400 cm³/min flow of 0.1% NO, 4% O₂, and balance He over 4 g of catalysts.

RESULTS AND DISCUSSION

NO Reduction

Supports. Four carbon-supported Cu catalysts were tested for the selective reduction of NO at 150 °C. BET surface area measurement was carried out for those carbons. The surface areas ranged from 90 m²/g to 943 m²/g. The activities for NO selective reduction with acetone were investigated in the presence of O₂. The activity over Rheinbraun AG, with the lowest surface area (90 m²/g), was the lowest among the carbons tested. The activity for NO conversion was much better for GmbH from Carbo-Tech with surface area of 440 m²/g. The initial NO conversion for Carbo-Tech carbon was high, but decreased to ~20% after 5 h. PCB from Calgon (927 m²/g) and GI of B&S (943 m²/g) carbons were the two best catalysts for NO reduction with acetone in the presence of O₂. The NO conversions were 26% and 32% after 5 h for GI and PCB, respectively. The results indicate that carbon materials with higher surface area would be better for NO selective reduction with acetone in the presence of O₂. Although the surface area of GI was about the same as PCB, the activity of PCB was somehow more stable than GI. This result suggests that the surface area was not the only factor affecting the activity of carbon catalysts for NO reduction. Factors such as pore size and Cu dispersion could influence the catalytic activity and the stability of reaction.

Reductants. Because the NO reduction activity of PCB was the best among the carbon materials tested, further investigation was focused on supported PCB catalysts. The NO conversion over 5%Cu-2%Ag/C with various hydrocarbons as reductants in the presence of O₂ and H₂O is shown in Table 1, along with the results in the absence of any hydrocarbon. The efficiency order of reductant was acetone>2-propanol>isobutanol>ethyl ether>propene, ethanol>methanol. The major NO reduction product was N₂ with >99% selectivity. Acetone was the most active reductant for NO selective reduction in the presence of O₂ and H₂O over the 5%Cu-2%Ag/C catalyst at 150 °C. The NO conversion with acetone was 35% with 3,000 h⁻¹ space velocity after 5 h on stream. Interestingly, the NO conversion without any reductant was higher than the conversion using propene, ethanol, or methanol as reductant. The results suggest

that propene, ethanol, and methanol inhibit the direct reduction of NO with carbon which is known as catalyzed by Cu in the presence of O₂.

The necessity of oxygen to promote the reduction of NO by acetone is shown in Figure 1. The NO conversion was low in the beginning and decreased to ~10% after 20 min on stream for the reaction without the presence of O₂. With 1% of O₂, NO conversion was high and slowly decreased to a steady level. With O₂ concentration of 4%, the reduction activity followed the same trend except with higher NO conversion. This shows that the reaction of NO directly with acetone is not significant in comparison with the NO selective reduction in the presence of O₂. Under the reaction conditions, the fast decrease of NO conversion during the first hour is not due to the NO adsorption on carbons since the conversion is also low in the absence of O₂. It is also unlikely that the decrease of NO conversion is caused by the adsorption of NO₂ since NO₂ decomposes quickly to NO on the surface of carbons.

Effect of H₂O and SO₂. Most literature shows an inhibiting effect of H₂O on NO reduction over various catalysts, e.g., Cu-ZrO₂ [4] and Co-ZSM-5 [1]. In contrast, results on 5%Cu-2%Ag/C showed that H₂O had no effect on NO reduction. The conversion of NO with 8% H₂O or without H₂O was essentially the same. Probably the highly hydrophobic property of carbon material surface prevents the interference of H₂O. SO₂, on the other hand, has a large negative effect on NO selective reduction with acetone. As shown in Figure 2, the catalyst deactivated very fast with 0.1% of SO₂. It is suspected that the presence of SO₂ poisons the metals by the formation of metal sulfates which deactivate the NO reduction activity.

Effect of Metals. Carbon alone is known as a catalyst for the selective reduction of NO with ammonia [5]. Figure 3 shows the NO conversion versus time for the carbon alone and for the 5%Cu-2%Ag/C catalyst. The enhancing effect of Cu+Ag on the activity of active carbon for NO conversion can be clearly seen with acetone as a reductant. The NO conversion decreased rapidly on active carbon alone (without Cu+Ag) with acetone in the presence of O₂ and H₂O. NO conversion was negligible after 1 h of reaction. On the other hand, the NO conversion over 5%Cu-2%Ag/C slowly decreased to 35% after 5 h. The results show that acetone in the absence of oxygen is not an effective reductant for NO reduction and it suggests that the function of Cu+Ag is to promote the oxidation of acetone for the selective reduction of NO. All experiments, with one exception, over 5%Cu-2%Ag/C in the presence of O₂ showed nearly 100% N₂ selectivity, i.e., no N₂O was formed. The only exception was the NO reduction with acetone in the absence of O₂, which showed >80% N₂O selectivity, suggesting that the NO reduction pathway in the presence of O₂ is different from the pathway in the absence of O₂. The formation of N₂O is probably from the direct reaction between NO and acetone or from the disproportionation of NO [6]. The high selectivity of the 5%Cu-2%Ag/C catalyst may be related to low catalyst activity for the activation of molecular oxygen, as observed on some solid acid catalysts [7]. Other metals supported carbon catalysts, such as Pt and Pd, were also tested for NO selective reduction with acetone. However, the NO reduction activity over Pt and Pd supported catalysts was much lower than the activity with Cu+Ag. Besides lower NO reduction activity with Pt and Pd, lower selectivity to N₂ was also noticed.

NO Oxidation

Active Carbon Fibers vs Active Carbon. Both the activated carbon fibers (ACFs) and PCB active carbon showed high NO oxidation activities at low temperature. The results are summarized in Table 2. At 30 °C with 400 ppm NO, 4% O₂, and balance He, NO conversions are 90% and 82% over ACF and active carbon, respectively. The activity, however, decreases with the temperature. At 75 °C, the NO oxidation conversion decreased to 51% and 42% on active carbon fibers and active carbon, respectively. Negligible oxidation was observed at 120 °C. This is consistent with results reported by Machida et al. [8]. The oxidation activity of both active carbon fibers and active carbon are interesting. Figure 4 shows the NO_x concentration versus time during NO oxidation reaction over active carbon at 30 °C. In the beginning, the adsorption of NO_x is severe. The concentration of NO increased with time and no NO₂ was detected for the first 7 h. After 7 h, NO₂ adsorption sites were saturated and as a result NO₂ breakthrough was observed. This suggests that NO₂ is adsorbed more strongly than NO on carbon materials.

Effect of Pretreatment. Three different pretreatments were tested to increase the NO oxidation activity of active carbons including heat treatment at 800 °C in N₂, reduction with H₂ at 800 °C, and oxidation using HNO₃. The results are shown in Table 3. None of the pretreatments increased NO oxidation at 120 °C. As reported by Machida et al. [8], the heat treatment increased the oxidation activity of active carbon fibers for NO to NO₂ in the presence of H₂O. It is speculated that the increased oxidation activity of fibers is from the formation unsaturation of carbon surface by the liberation of CO and CO₂ with the heat treatment in N₂. The removal

of the oxygen functional group, which increases the hydrophobic nature of the carbon, also contributes to the increase in NO oxidation activity of carbons in the presence of H_2O . However, as shown in Table 3, the heat treatment actually slightly decreased the oxidation activity of the PCB active carbon at 75 °C. The NO oxidation activity decreased from 42% to 35% at 75 °C after the heat treatment.

It was reported that H_2 reduction at high temperature was able to reduce the oxygenated functional groups on carbons [9]. The active carbon pretreated with H_2 was then tested for NO oxidation. The activity, also shown in Table 3, was negligible at 120 °C. The oxidation activity at 75 °C was close to the activity after the heat treatment and was lower than the catalyst without pretreatment. Both heat treatment and H_2 reduction treatment were intended to remove the oxygenated functional groups on carbon and to improve the oxidation activity. However, the results showed a negative effect on NO oxidation to NO_2 . The results of active carbon for NO oxidation after the HNO_3 treatment are also included in Table 3. The activity was negligible at 120 °C and was only 28% at 75 °C.

All pretreatments resulted in some negative change of the activity of activated carbons for NO oxidation, indicating that the functional groups alone do not play the major role in the NO oxidation reaction. It is possible that the cooperative relationship between oxygenated functional groups and nonoxygenated functional groups is important for NO oxidation to NO_2 .

Effects of SO_2 and H_2O . The effect of SO_2 on NO oxidation activity over heat-treated PCB active carbons was studied by adding 0.1% SO_2 to the inlet gas. The results are also shown in Table 3. The NO oxidation activity was negligible in the presence of SO_2 over the catalyst at 120 °C. When the reaction temperature was further decreased to 75 °C, no oxidation activity was observed as compared to 35% NO oxidation conversion in the absence of SO_2 . The result suggests that the presence of SO_2 poisoned the oxidation activity of carbon catalysts, which is similar to the results reported in the literature [10-12]. The competitive adsorption of NO and SO_2 on carbon surfaces is possibly the cause.

We also tested the combined effect of SO_2 and H_2O on the active carbon for NO oxidation. As reported earlier [13], SO_2 greatly promotes the NO oxidation reaction in the presence of H_2O over Co/Al_2O_3 . However, the NO oxidation activity was negligible over the active carbon in the presence of SO_2 and H_2O at 120 °C.

Active Carbon Supported Catalysts. Five percent cobalt oxide and 1% iron oxide supported on active carbons were tested for NO oxidation. The results are summarized in Table 4 to compare with the NO oxidation activity of unsupported active carbon. Again, both active carbon-supported catalysts showed negligible activity at 120 °C. It is believed that the decomposition activity of carbons for NO_2 to NO is too fast at 120 °C to be overcome by the oxidation activity of metal oxides. The activities at 75 °C were obtained followed by the tests at 120 °C. The NO oxidation activities were 26% and 24% over 1% iron oxide/A.C. and 5% cobalt oxide/A.C., respectively. The activities of active carbon-supported catalysts were lower than the unsupported catalyst at 75 °C.

CONCLUSIONS

Acetone was the most active reductant for NO selective reduction over 5%Cu-2%Ag/C among the hydrocarbons tested. Acetone, oxygen, and carbon-supported Cu+Ag catalyst are all required to maintain high NO conversion and high N_2 selectivity at these low temperatures. Although 35% NO conversion is relatively high at 150 °C in the presence of O_2 and H_2O , further improvement is needed for the process to be competitive with other processes. The NO reduction activity of Cu-Ag/carbon with acetone was also greatly decreased by the presence of 0.1% SO_2 , which may be present even downstream of some flue gas desulfurization systems.

Both active carbon fibers and active carbon are active for NO oxidation to NO_2 at low temperature. At 30 °C and 0.01 g-min/cm³ space velocity, the NO conversions to NO_2 were 90% and 82% on active carbon fibers and active carbon, respectively. However, the activity decreased with the temperature, becoming negligible at 120 °C on both active carbon fibers and active carbon. Different treatments (heat treatment at 800 °C, reduction in H_2 , and oxidation with HNO_3) and additional metals did not improve the NO oxidation activities of carbons at 120 °C. With the addition of 0.1% SO_2 , the NO oxidation activity of activated carbon was poisoned and the conversion was negligible at 75 °C.

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Table 1. NO Selective Reduction by Hydrocarbons over 5% Cu-2% Ag/C (1,000 ppm NO, 4% O₂, and 8% H₂O, 3,000 h⁻¹, 150 °C)^a

Reductant	NO Conversion (%)	N ₂ Selectivity (%)
0.13% acetone	35	>99
0.13% 2-propanol	31	>99
0.10% isobutanol	25	>99
0.08% ethyl ether ^b	18	>99
0.20% ethanol	<10	>99
0.11% propene	<10	>99
0.40% methanol	negligible	>99
none	11	>99

^a All catalysts subjected to He treatment at 400 °C for 1 h before reaction. The conversion and selectivity was taken after 5 h on stream.

^b The concentration of ethyl ether was limited by its solubility in water.

Table 3. NO Oxidation to NO₂ over PCB Active Carbon (A.C.)

PCB A.C.	Temperature	
	120 °C	75 °C
Fresh	negligible	42%
Heat treatment	negligible	35%
H ₂ reduction	negligible	31%
HNO ₃ oxidation	negligible	28%
With 0.1% SO ₂	negligible	negligible
With 0.1% SO ₂ + 10% H ₂ O	negligible	not available

Note: Activities at 120 °C were obtained after 24 h on stream and the activities at 75 °C were obtained after 24 h at 120 °C and 40 h at 75 °C. Reaction conditions: 400 ppm NO, 4% O₂, and balance He; 400 cm³/min over 4.0 g of catalysts.

Table 2. NO Oxidation to NO₂ over Active Carbon Fibers (ACF) and PCB Active Carbon (A.C.)

Carbon	Temperature		
	30 °C	75 °C	120 °C
ACF	90%	51%	negligible
PCB A.C.	82%	42%	negligible

Note: Activities were obtained after 40 h on stream. Reaction conditions: 400 ppm NO, 4% O₂, and balance He; 400 cm³/min over 4.0 g of catalysts.

Table 4. NO Oxidation to NO₂ over PCB Active Carbon (A.C.) and Active Carbon-Supported Catalysts

Catalyst	Temperature	
	120 °C	75 °C
Fresh A.C.	negligible	42%
1% iron oxide A.C.	negligible	26%
5% cobalt oxide A.C.	negligible	24%

Note: Activities at 120 °C were obtained after 24 h on stream and the activities at 75 °C were obtained after 24 h at 120 °C and 40 h at 75 °C. Reaction conditions: 400 ppm NO, 4% O₂, and balance He; 400 cm³/min over 4.0 g of catalysts.

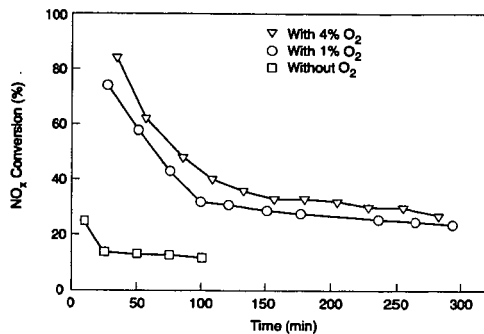


Figure 1. NO conversion over 5%Cu-2%Ag/C as function of time with different O₂ concentration. Reaction conditions: 0.1% NO, 0.13% acetone, 8% H₂O at 150 °C with 3,000 h⁻¹ space velocity.

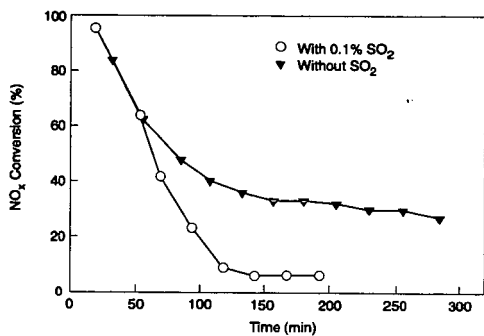


Figure 2. The effect of SO₂ on NO reduction with acetone over a Cu supported carbon catalyst at 150 °C; 0.1% NO, 0.13% acetone, 4% O₂ and 8% H₂O; 3,000 h⁻¹.

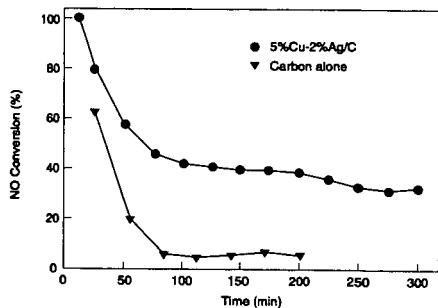


Figure 3. NO conversion versus time over 5%Cu-2%Ag/C and carbon only. Reaction conditions: 1,000 ppm NO, 8% H₂O, 3,000 h⁻¹, 150 °C.

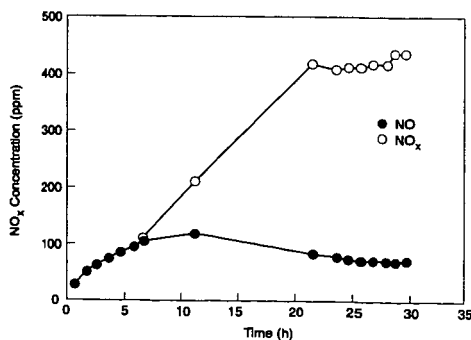


Figure 4. NO and NO_x concentrations as function of time during NO oxidation over activated carbon at 30 °C; 400 ppm NO, 4% O₂, and balance He; 400 cm³/min over 4.0 g of catalysts.